

A simulative comparison of dense and microporous membrane reactors for the steam reforming of methane

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Abstract

The steam reforming of methane using catalytic membrane reactors has been simulated for two types of membranes – a dense Pd/Ag composite membrane and a series of microporous membranes. Various values of hydrogen separation factors were investigated for the latter. In general the Pd/Ag membranes gave the better performance, for all parameters investigated including temperature, pressure, sweep ratio, and membrane thickness. However, the use of steam as a sweep gas produced an improved performance for the microporous membranes operating in the Knudsen region. © 1998 Elsevier Science B.V.

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1. Introduction

According to Scholz [1], global annual production and utilisation of hydrogen now totals some $5 \times 10^{11} \text{ Nm}^3$, of which 48% is produced from natural gas. The main process of producing hydrogen from natural gas or methane is by steam reforming. Steam reforming is a highly endothermic process carried out by passing a mixture of steam and natural gas over a catalyst packed into tubes of high temperature alloys of small diameter in order to facilitate heat transfer. Because the steam-reforming reaction is equilibrium limited and endothermic, high temperatures must be employed to achieve a high conversion of methane. Temperatures of up to 850°C are commonly achieved for the reaction with steam-to-methane ratios in the

range of 2.5 : 1 to 4.1 and pressures ranging from 1 to 4 MPa. Use of elevated pressure enables the energy efficiency of the process to be improved. Under these conditions the conversion of methane is $\approx 80\%$, the limitation being a result of the equilibrium constraint.

One possible way to liberate this reaction from the equilibrium limitation and thus attain a high methane conversion at lower temperature is by the use of membrane reactors. By employing a hydrogen selective membrane, the hydrogen produced by steam reforming is removed from the reaction zone so that the chemical equilibrium shifts towards a higher reactant conversion. Based on this concept, reactors in which separation membranes are incorporated have been proposed and investigated for the steam-reforming reaction [2,3].

Because of the well-known ability of palladium or palladium alloys to permeate hydrogen with 100% permselectivity the first developments were made with

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very thin wall thicknesses of these metals. Thus, Laegsgaard Jorgensen et al. [4] used a metal tube of Pd-23% Ag of 0.1 mm thickness to study the steam-reforming reaction. In order to obtain even thinner Pd or Pd/Ag layers to facilitate hydrogen permeation, recourse has been made to deposition of thin films of these materials onto porous supports. The supports used include porous glass and ceramics [5–7] or porous metals [8] with deposition of the Pd by magnetron sputtering or electroless plating techniques. The use of supported precious metal films is preferred because of the high hydrogen flux requirement which cannot be attained with most currently available dense metal membranes because of their thickness.

An alternative to the precious metal type of membrane is the microporous membrane, which typically contains a separation layer with pores of a few nanometres in diameter and which achieves separation by a Knudsen or similar diffusional process. Such membranes have been investigated for the steam-reforming reaction by a number of investigators including Tsotsis [8,9] and Chai et al. [10].

However, despite extensive studies of membrane reactors and their merit as a means of overcoming the equilibrium limitation of a number of reactions of commercial interest, there has been no detailed comparison of the two main types of membrane for this particular reaction. In the present paper, a simulation study is presented which compares the performance of composite Pd/Ag and microporous ceramic membrane reactors based on a laboratory-scale model. The main variables influencing membrane reactor performance including sweep gas-flow rate, temperature, pressure and membrane selectivity, are investigated and discussed.

2. Mathematical model

The following assumptions were made for the formulation of the mathematical model used in the present work:

1. The reaction is conducted isothermally.

As the reaction is highly endothermic, this assumption may not be completely justified. However, the proposed use of a sweep gas can supply sufficient heat necessary to maintain an approximately constant reaction temperature.

2. Negligible pressure drop occurs along the length of the reactor. Several studies conducted with this type of reactor have shown the validity of this assumption, e.g. Collins et al. [11].
3. Axial and radial dispersion are assumed to be negligible. Previous studies by us [12] have established that radial dispersion is negligible with the current reactor geometry. Axial dispersion can be neglected provided the bed length to particle diameter ratio is great than 50 as in the present system [13].
4. The permeation of hydrogen through the palladium/silver membrane follows Sievert's law [14], i.e. the driving force is proportional to the difference in the square roots of the feed and permeate pressures.
5. Knudsen diffusion is the only mode of transport through the microporous membrane. Hence, the selectivity of the membrane is calculated in terms of the square roots of the inverse molecular weights of the permeating molecules.
6. Cocurrent flow only considered.

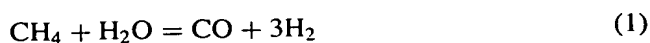
The mathematical model of the present system consists of conservation equations for each component on the feed and permeate side of the membrane written for a differential reactor length. These equations consist of convection, permeation and reaction terms. With the assumptions specified above and at steady state, these equations can be written as:

$$\frac{dN_i}{dl} = \nu_i R - P_i$$

where R is the reaction rate (equal to zero for the permeate side), ν_i the reaction stoichiometry for component i and P_i the component permeation rate.

The system of differential equations, of an initial value type was solved using the LSODE solver [15].

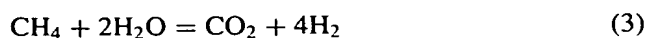
The kinetic parameters used for the steam reforming of methane are those given by Xu and Froment [16] as these are, generally, considered to be the most reliable in the literature. These rate expressions were expressed in the form of Langmuir–Hinshelwood kinetics for the three main reactions as follows:



$$R_1 = \frac{k_1}{P_{\text{H}_2}^{2.5}} \left(P_{\text{CH}_4} P_{\text{H}_2\text{O}} - \frac{P_{\text{H}_2} P_{\text{CO}}}{K_1} \right) / (\text{DEN})^2$$



$$R_2 = \frac{k_2}{P_{\text{H}_2}} \left(P_{\text{CO}} P_{\text{H}_2\text{O}} - P_{\text{H}_2} \frac{P_{\text{CO}_2}}{K_2} \right) / (\text{DEN})^2$$



$$R_3 = \frac{k_3}{P_{\text{H}_2}^{3.5}} \left(P_{\text{CH}_4} P_{\text{H}_2\text{O}}^2 - P_{\text{H}_2}^4 \frac{P_{\text{CO}_2}}{K_3} \right) / (\text{DEN})^2$$

where $\text{DEN} = 1 + K_{\text{CO}} P_{\text{CO}} + K_{\text{H}_2} P_{\text{H}_2} + K_{\text{CH}_4} P_{\text{CH}_4} + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} / P_{\text{H}_2}$.

Hydrogen permeation data presented by Shu et al. [7] were used in the simulation for permeation rates through the palladium membranes.

3. Results and discussion

The data used for the simulation are presented in Tables 1 and 2. Table 1 gives the general properties of the permeator and the operating conditions employed, while Table 2 provides specific information relating to the types of membrane used. The Pd/Ag membrane is assumed to possess 100% permselectivity for hydrogen, whereas for the microporous membrane, the individual separation factors were based on Knudsen flow, with a value of 3.74 taken for the ideal H_2/N_2 selectivity under the present conditions.

The general effect of the removal of hydrogen on the equilibrium conversion of methane during steam reforming is illustrated in Fig. 1, where the percentage

Table 1
Membrane reactor data and operating conditions

Effective length of catalytic bed	100 mm
Diameter of catalytic bed	10 mm
Thickness of ceramic support	1 mm
Porosity of catalyst bed	0.5
Catalyst used	12% Ni/ Al_2O_3
Reaction temperature (base case)	773 K
Steam/methane ratio	3
Total feed gas-flow rate	0.1 dm ³ /min
Feed gas composition	CH_4 – 99% H_2 – 0.99% N_2 – 0.01%
Sweep gas-flow rate	0.4 dm ³ /min
Pressures	
– Feed (tube-side)	1.36 bar
– Sweep gas (shell-side)	1.0 bar (1.36 for microporous membrane)

Table 2
Individual data for Pd/Ag and microporous membranes

Pd/Ag membrane thickness	20 μm
Porous membrane porosity	0.2
Porous membrane pore diameter	4 nm

methane conversion is plotted against potential hydrogen removal, also given as a percentage. This plot (similar to that given by Shu et al. [7]), indicates the effectiveness of a membrane reactor in promoting increased conversion by removal of one of the products of the reaction. The different curves in Fig. 1 correspond to various temperatures of operation. It can be seen that hydrogen removal has little effect when the reaction is carried out at 700°C, but large extents of hydrogen removal considerably enhance the conversion of methane at lower temperatures. Thus for example, for operation at 400°C, removal of 60% of the hydrogen produced from the reaction mixture will increase the conversion of methane from the equilibrium level of 18 to 31%. Similar effects are obtained at other temperatures, with conversion of methane exhibiting major increases when the extent of hydrogen removal is greater than 60%. This feature points to the importance of having a membrane which has both the selectivity and capacity to remove substantial amounts of the hydrogen produced in the reaction.

The influence of temperature on both the Pd/Ag and the microporous membrane reactors is shown in Fig. 2, where both the methane conversion and the percentage improvement over the equilibrium level, obtained by using these membrane reactors is plotted as a function of temperature. For the purpose of comparison, the microporous membrane is shown with a value of 3.74 for the hydrogen selectivity; this specified information is indicative of a typical microporous membrane selectivity for the present reaction. An examination of the conversions obtained for the Pd/Ag membrane and the microporous membrane, and a comparison of these with the equilibrium values at various temperatures, shows that the Pd/Ag membrane gives the highest conversion at all temperatures, followed by the microporous membrane, which in turn produces a higher methane conversion than the equilibrium values. However, it should be noted that the improvement in conversion obtained by the Pd/Ag

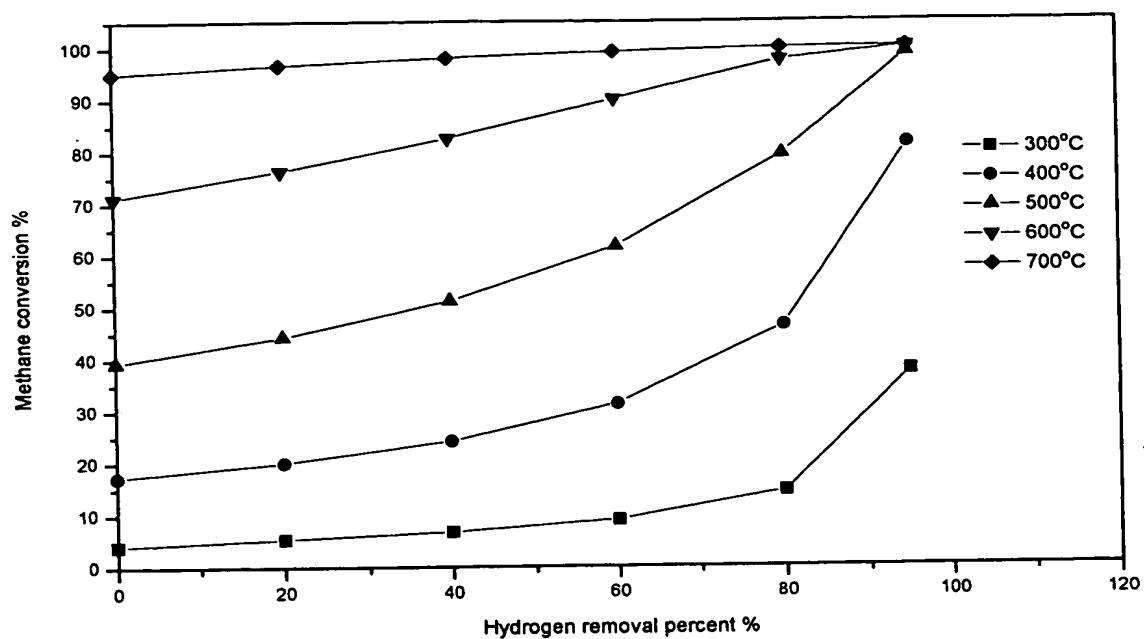


Fig. 1. Influence of hydrogen removal on the equilibrium methane conversion.

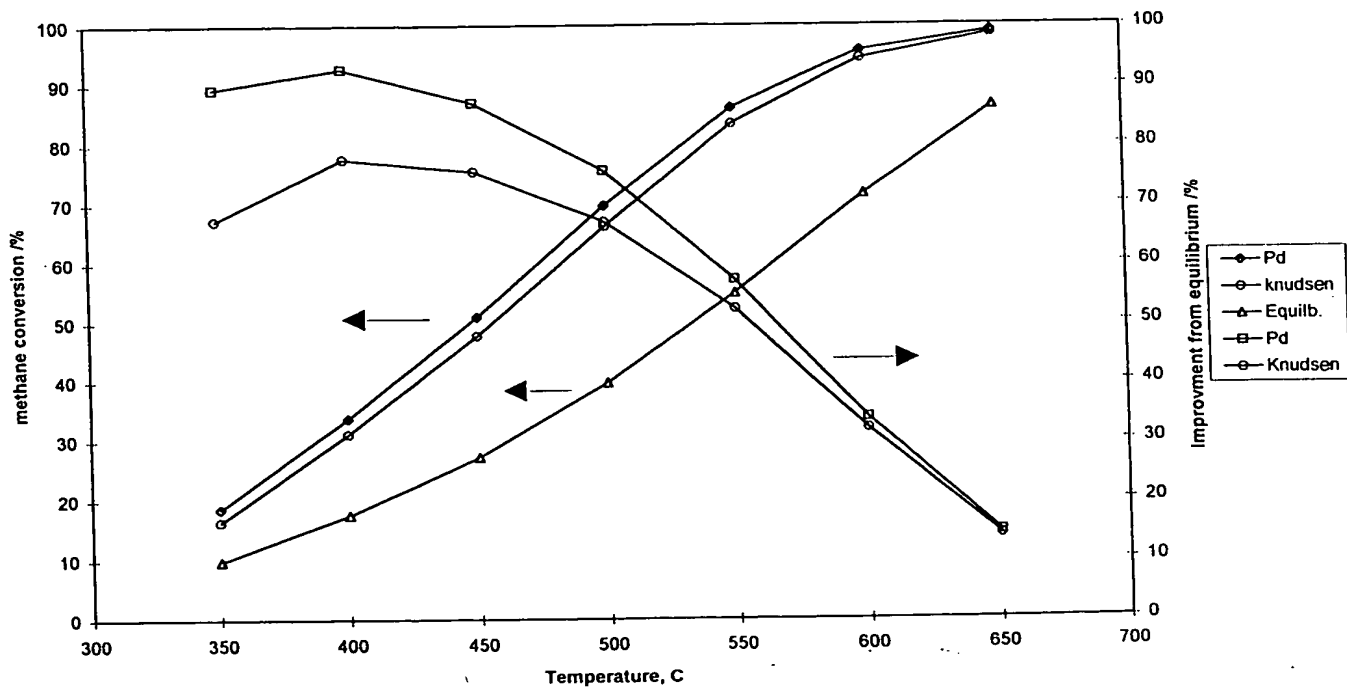


Fig. 2. Effect of temperature on methane conversion and improvement over the equilibrium level for Pd/Ag and microporous membrane reactors.

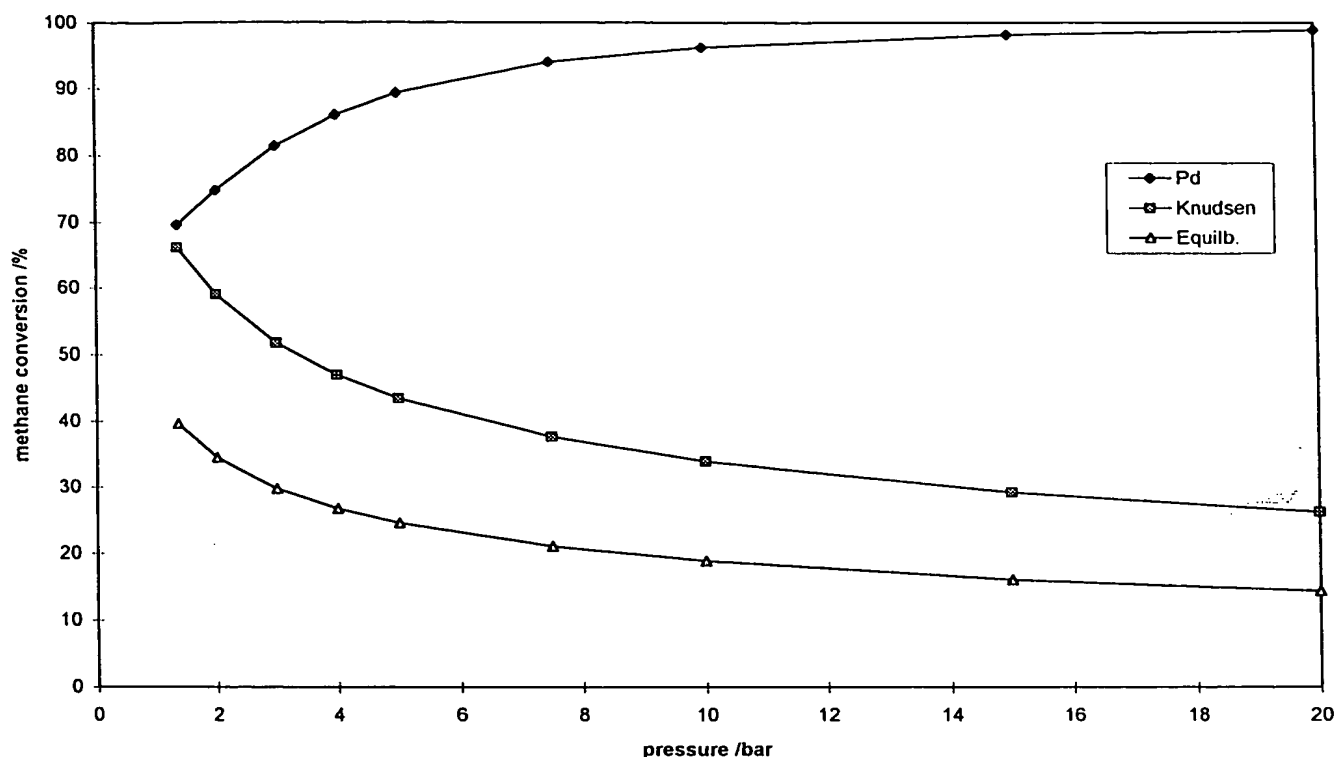


Fig. 3. Effect of pressure on methane conversion for Pd/Ag and microporous membrane reactors.

membrane compared with the microporous membrane (and indeed over the equilibrium level) is greatest in the mid-temperature range, i.e. between 450 and 600°C. At higher temperatures all three curves tend to coincide, due to the lesser influence of hydrogen removal in this temperature region as noted from the results in Fig. 1. At lower temperatures, the conversion with the microporous membrane tends to converge to the equilibrium values, but the Pd/Ag membrane also tends to give slightly lower conversions.

The effect of hydrogen removal on conversion is demonstrated more explicitly in the same figure by plots of improvement over the equilibrium level for both membrane reactors. The extent of these improvements is shown as percentages on the right-hand side of Fig. 2. It can be seen that at temperatures ca. 400–450°C the conversion of methane is almost doubled compared to the equilibrium values, whereas the microporous membrane gives an increased conversion of ca. 25% only.

In a conventional reactor an increase of pressure leads to a decreased conversion of methane during the steam-reforming reaction, as shown by the curve for the equilibrium in Fig. 3. These results are for a temperature of 500°C. A similar reduction in conversion with temperature is obtained for the microporous membrane with a selectivity of 3.74 with respect to hydrogen, albeit with levels of conversion higher than equilibrium. However when the Pd/Ag membrane is employed, the conversion increases with pressure due to selective removal of hydrogen by permeation with increase of pressure for this membrane.

A comparison of the microporous membrane performance for different selectivity values for the membrane is given in Fig. 4, where the conversions obtained for both the Pd/Ag and the microporous membranes are plotted as a function of the sweep ratio, i.e. the ratio of sweep gas-flow rate to the feed-flow rate. This ratio was varied from 0 to 5 for all membranes. In this figure, the selectivity factors for the microporous membranes refer to the H_2/N_2 value

Effect of Sweep Ratio on Methane Conversion

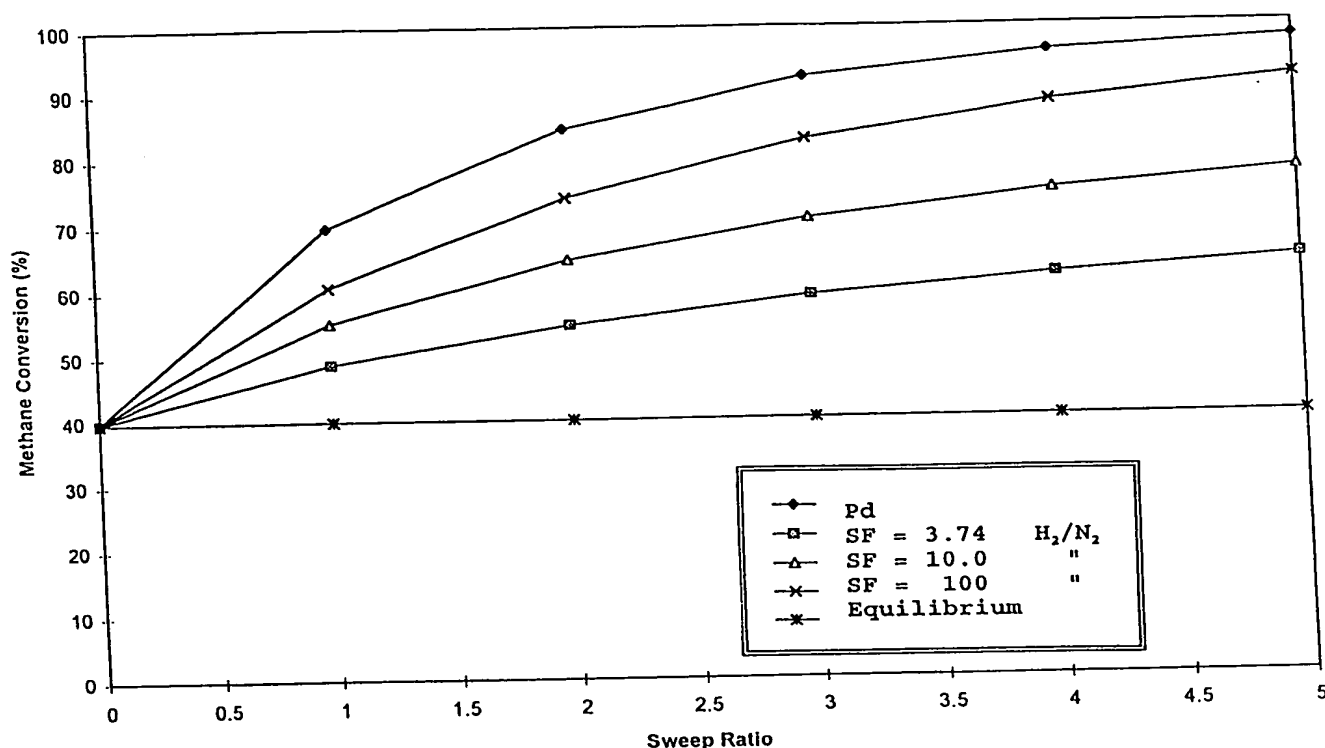


Fig. 4. Pd/Ag and microporous membrane performance as a function of the sweep/feed flow. N_2 as sweep. Hydrogen separation factors as parameter for microporous membranes.

which is taken as a reference. The results in Fig. 4 are for the case where nitrogen is used as sweep gas. For the microporous membranes in which the hydrogen selectivity was assumed to be higher than the Knudsen value of 3.74, values of 10 and 100 for the hydrogen selectivity were assumed. This assumption may not be completely accurate, as it is usually the case that when the selectivity improves, the permeation rates of all components (including hydrogen) decrease. Nevertheless, a broad picture of the effect of increased selectivity can be obtained with the assumption given above. Fig. 4 shows that an extremely high methane conversion can be obtained at the assumed operating temperature of 500°C, by using a membrane with high selectivity to hydrogen (above 100) with the highest level achieved using the Pd/Ag membrane which possesses 100% selectivity to hydrogen. However, this high conversion could only be achieved at a high

sweep ratio, with a corresponding problem of hydrogen separation from the sweep gas.

The problem of separation of the useful product (hydrogen in the present case) from the permeate stream in which a large quantity of inert gas is used for the sweep gas can be reduced if steam is used as a sweep gas. The advantages of steam as a sweep gas include:

- (a) usually available on site;
- (b) separation from the combined sweep stream is relatively easy (condensation); and
- (c) a high heat capacity.

Fig. 5 is a similar plot to Fig. 4 but now steam is used as a sweep gas. A comparison with Fig. 4 shows that the presence of steam as the sweep gas considerably enhances the conversion of methane for low values of the hydrogen/nitrogen separation factor. This is brought out more clearly in Table 3, where

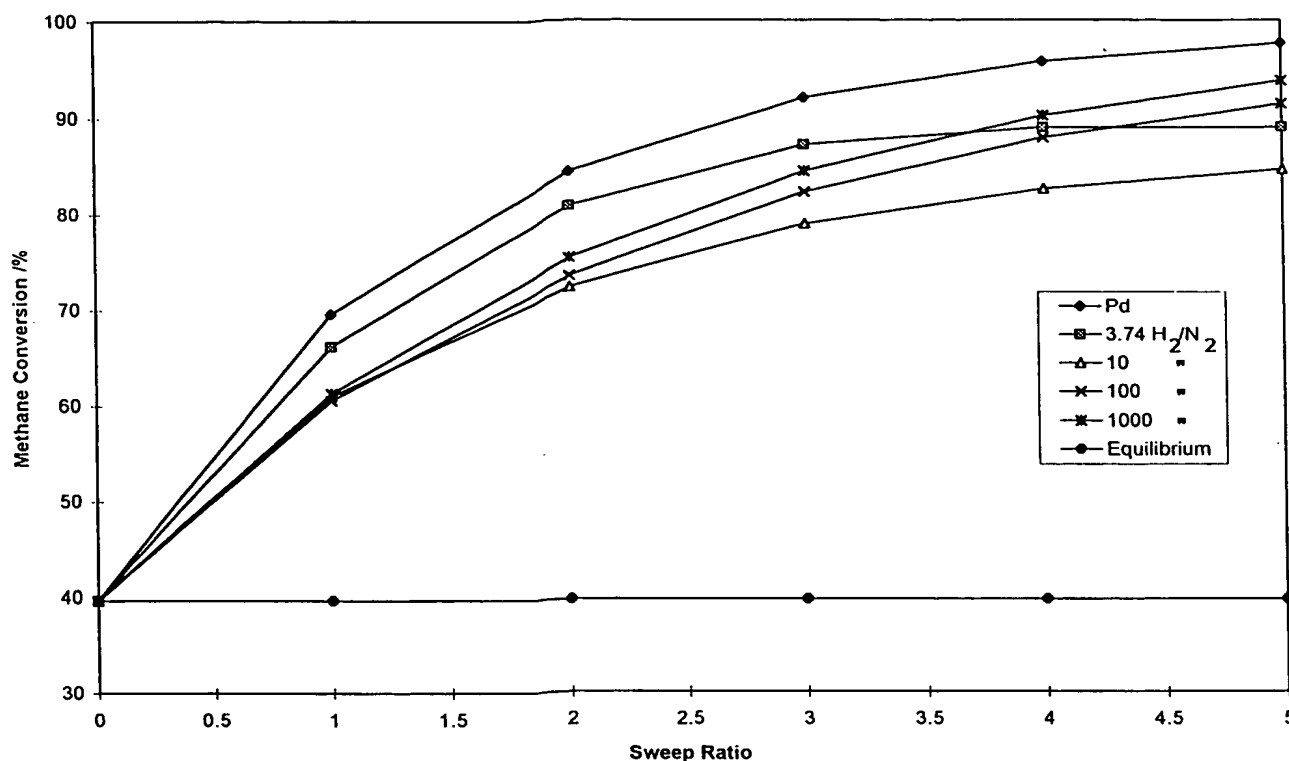


Fig. 5. Pd/Ag and microporous membrane performance as a function of the sweep/feed flow. Steam as sweep. Hydrogen separation factor as parameter for microporous membranes.

Table 3
Comparison of efficiencies of nitrogen and steam as sweep gases on methane conversion

Methane conversion %						
Sweep ratio	Separation factor					
	3.74		10.00		100.00	
	N ₂	Steam	N ₂	Steam	N ₂	Steam
1	47	65	53	60	59	61
2.5	53	85	65	73	75	76
4.0	59	87	71	81	85	85

the methane conversion is compared for nitrogen and steam as sweep gases for values of the sweep ratio from 1 to 4 and for separation factors of 3.74, 10 and 100. Considering first of all the effect of separation factor it can be seen that as this is increased from 3.74 through 10 to 100 the differences between the use of nitrogen and steam as sweep gases diminishes. Thus at a separation factor of 3.74 and a sweep ratio of 1, the

methane conversion is increased from 47 to 65% on substituting steam for nitrogen as the sweep gas; a difference of 18%. However, when the separation factor is increased to 10 and 100 the corresponding differences in conversions between nitrogen and steam sweep gases decrease to 7 and 2%, respectively. This effect is perpetuated for the other two sweep ratios of 2.5 and 4.0.

This apparently anomalous behaviour, in which the beneficial effect of steam diminishes as the separation factor increases, is due to the back permeation of steam from the sweep, or permeate side, of the membrane to the tube side where reaction occurs. This will increase the steam-to-methane ratio and favour increased conversion of methane. A membrane separation with a factor of 3.74 will have an increased steam back permeation rate compared to membranes with the higher separation factors of 10 and 100 and hence provide a greater enhancement of methane conversion.

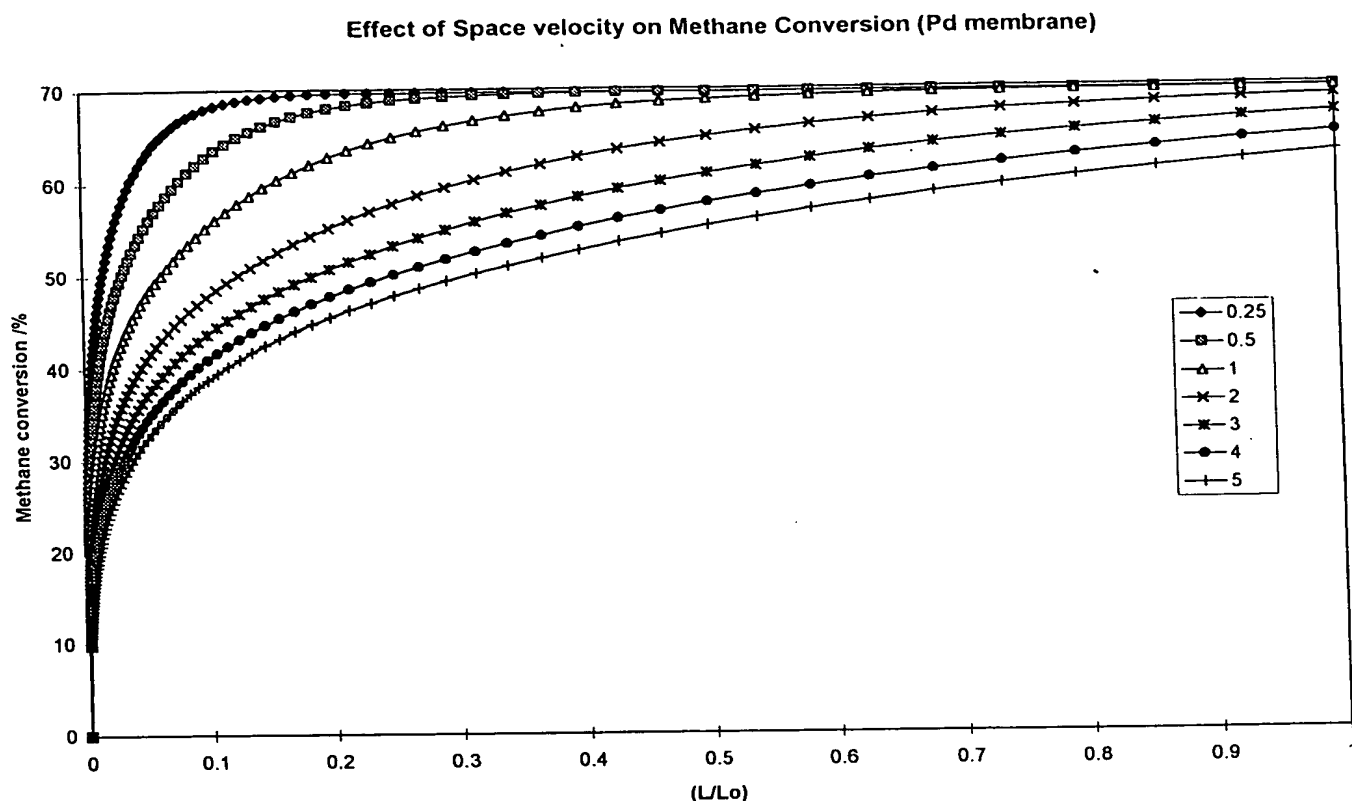


Fig. 6. Effect of space velocity on membrane conversion for Pd/Ag membranes.

The effect of space velocity on methane conversion for the Pd/Ag membrane is illustrated in Fig. 6. In this figure, the space velocity is presented as ratios of the sweep flow to the feed flow. The figure shows the conversion at different space velocities as functions of the dimensionless reactor length ratios based on the standard value of unity. As expected in all cases a high space velocity gives a lower conversion for the Pd/Ag membranes. There is a sharp initial rise in conversion on progression along the reactor, followed by a less dramatic conversion increase. A similar plot is obtained for the microporous membrane (not shown) but with a slightly lower conversion in the inlet region of the reactor compared to the Pd/Ag membrane. Thus a conversion of 69% was attained by the Pd/Ag membrane at a dimensionless reactor length of 0.15 for a space velocity ratio of 0.25, whereas at the same point in the reactor the microporous membrane with the same space velocity ratio achieves a conversion of 65% only. However, as the space velocity is increased

the difference between the two membranes becomes insignificant.

One consideration, which is important, relates to membrane thickness; this is especially so for the Pd/Ag membranes, where the cost of the precious metal could be a significant factor in the costs of the membrane. Fig. 7 shows plots of the methane conversion against membrane thickness over the range from 1 to 18 μm . This is the range of thickness usually obtainable for both the precious metal layers and also for the separation layer of microporous membranes. Two values are taken for permeation in the Pd/Ag layer. The first, designated as Pd membrane A, has the values reported by Gobina et al. [17] and by Govind and Atnoor [18] with a hydrogen permeation constant value of $7.174 \times 10^{-5} \exp(-767/T)$. The Pd membrane designated B has a constant equal to $0.049 \exp(-1888/T)$ as reported by Shu et al. [19] and Kikuchi and Uemiya [20]. Both constants are in units of $\text{cm}^2 \text{s}^{-1} \text{bar}^{-1/2}$. Fig. 7 shows that for the micro-

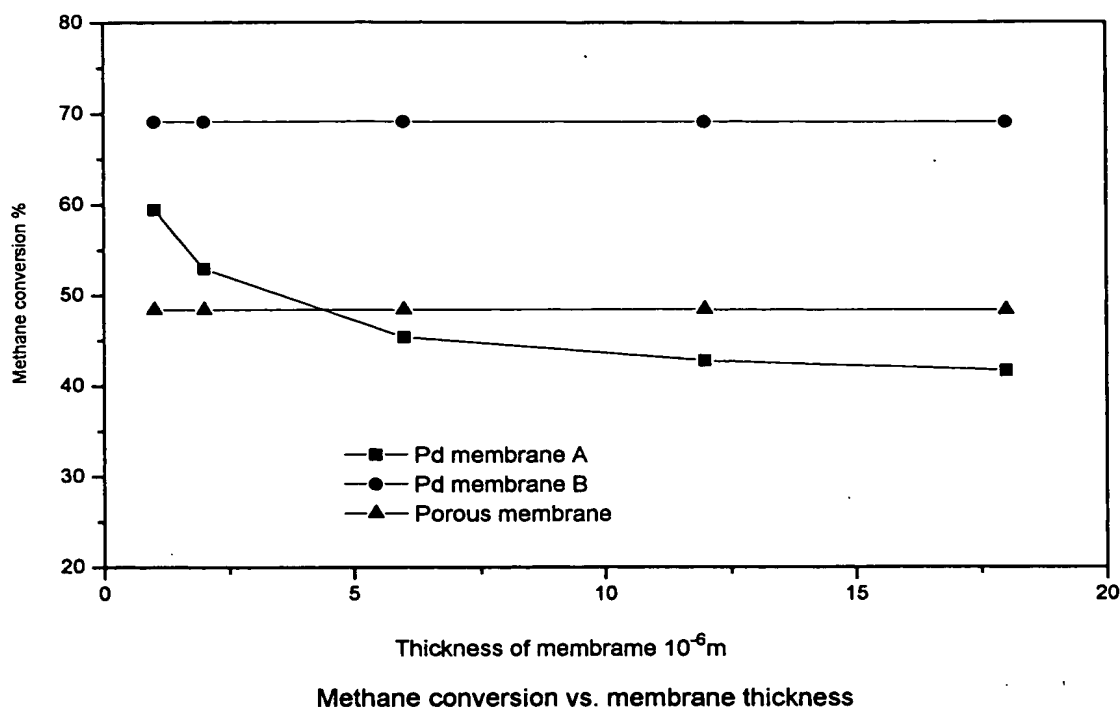


Fig. 7. Influence of membrane thickness on methane conversion.

porous membrane and Pd membrane B variation of membrane thickness from 1 to 18 μm has no effect on conversion with the Pd membrane giving a conversion of 69% while the microporous membrane gave a conversion of 49%. Standard conditions were used for this comparison. However, when the Pd membrane A was used, a sharp fall in conversion occurred as the membrane thickness increased from 1 to 6 μm , the conversion finally levelling off at ca. 40%. These results may be explained as follows. Because of the high hydrogen permeability of membrane B, the partial pressure of hydrogen will rapidly become equal on both sides of the membrane. An increase in thickness of the membrane will only result in the position at which this equivalence occurs to move downstream in the reactor. Thus no effect is observed on the methane exit conversion. For the microporous membrane, a similar effect occurs but because of the comparative non-selective nature of the membrane, equivalence of all species is attained on both the feed and shell sides. Permeabilities are now so high that an increase in thickness over the range cited has no effect on methane conversion. With the Pd/Ag membrane A,

a sharp drop in conversion occurs when the membrane thickness is increased sixfold from 1 to 6 μm . However, with further increase of thickness a reduced drop in conversion with membrane thickness is observed because the relative thickness ratio is now reduced. These results indicate the importance of obtaining reliable and appropriate data for the hydrogen permeability when Pd/Ag membranes are to be used.

4. Conclusions

The steam reforming of methane in a catalytic membrane reactor has been simulated using a relatively simple model in order to identify the major parameters influencing the conversion of methane. Two types of membrane were considered, namely a Pd/Ag dense composite membrane and a microporous membrane. For the latter, a range of values of the separation factor were modelled in order to determine the effect of membranes with properties equal to and superior to the Knudsen transport process. The effect of pressure has been shown to be dependent on the

type of membrane, while the potential benefits of using steam as a sweep gas have also been investigated. It has been demonstrated that the effect of varying the membrane thickness is strongly dependent on the permeability values for the Pd/Ag membranes.

Acknowledgements

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